

Effect of Temperature on Capillary Pressure

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The effect of temperature on capillary pressure is one of several fascinating problems unearthed by J.R. Philip during his long career. In his classic paper written with Daniel de Vries, he assumed reasonably, but incorrectly, that the relative change in capillary pressure with temperature was equal to that of the surface tension of water. In fact the change for capillary pressure is roughly four times as large. Four mechanisms may be proposed to explain this discrepancy: expansion of water, expansion of entrapped air, solute effects on the surface tension of water, and temperature-sensitive contact angles. None of these explanations describes all of the pertinent data. A definitive explanation appears to be as elusive today as it has been at any time.

1. INTRODUCTION

John Philip's intellect, creativity, and productivity were so protean that his body of work can be viewed as a scientific bulldozer that created a vast terrain of important results but simultaneously left numerous lesser, but fascinating, problems for his grateful successors to examine in detail. An illustrative example of this simile is the subject of this chapter: the effect of temperature on capillary pressure, which was a minor point in a short (yet, nonetheless, very influential) paper that Philip published with Daniel de Vries in 1957.

Three aspects of *Philip and de Vries* [1957] are notable. First, given the problem addressed, the paper is astonishingly short, a scant ten undersize pages. (This chapter, one of many that have dwelt on a single equation in the paper, is three times as long.) Second, the paper has been extremely influential both in geophysics but no less so in engineering. A recent computerized inquiry for citations of the paper found 473 citations—a statistic that undoubtedly underestimated the influence of the paper. Given the paper's age, many modern authors have no doubt cited intermediate works without citing (or knowing) the original, seminal work. The third and most fascinating aspect is that both authors largely abandoned the topic with this paper. After leav-

ing CSIRO, de Vries became a physics professor in his native Netherlands. While his professional obligations compelled him to work on other problems, de Vries retained an affinity and interest in the subject. (After his retirement he wrote a review paper revisiting the topic in which he quoted touchingly the French, *On revient toujours à ses premières amours* [de Vries, 1987].) Aside from a paper written during a second visit by de Vries nearly thirty year later, Philip appears not to have considered the problem further [de Vries and Philip, 1987].

In *Philip and de Vries* [1957] the authors developed what proved to be a seminal model describing the simultaneous transfer of energy, liquid water, and water vapor in an unsaturated, nonisothermal porous medium. To describe these processes, they needed to estimate the change in capillary pressure with temperature. *Philip and de Vries* [1957] turned naturally to the so-called Young-Laplace equation:

$$p_c = \frac{2\gamma^{\text{lg}} \cos \Theta}{r} \quad (1)$$

where p_c is capillary pressure (in pascals); Θ , the contact angle between the solid and the liquid-gas interface (in degrees); γ^{lg} , the liquid-gas interfacial tension (in newtons per meter); and r , the apparent pore radius (in meters). At that time it was well established that the water film thickness for agricultural soils above the permanent wilting point was equivalent to many molecular thicknesses [Taylor, 1958]. The conventional wisdom of the day held that the contact angle of a liquid-gas interface at a solid wetted with two or more molecular layers of water was zero. As will be discussed in Section 3.4.1, it has only recently become apparent that this conventional wisdom was fallacious. Accordingly, it was not merely expeditious, but reasonable also, to assume a zero contact angle at a porous solid so wetted and, accordingly, $\cos \Theta = 1$. Equation (1) then became:

$$p_c = \frac{2\gamma^{\text{lg}}}{r}. \quad (2)$$

Taking the total derivative of equation (2) with respect to temperature and dividing through by p_c , they obtained:

$$\frac{1}{p_c} \frac{dp_c}{dT} = \frac{1}{\gamma^{\text{lg}}} \frac{d\gamma^{\text{lg}}}{dT} \quad (3)$$

where T is temperature (in kelvins).

As the old chestnut says, “Complex problems have simple, easy-to-understand wrong answers,” and equation (3) appears to be wrong, on average, by a factor of 4. For soils studied $(1/p_c)(dp_c/dT)_{T=298\text{ K}}$ ranges

from -0.00172 to -0.02829 K^{-1} with an average value of -0.00844 K^{-1} , whereas $(1/\gamma^{\text{lg}}) (d\gamma^{\text{lg}}/dT)_{T=298 \text{ K}}$ for pure liquid water is -0.002135 K^{-1} [Grant, in press]. The difference is small but much too large and too consistently observed to be attributable to experimental error.

Interestingly, why equation (3) is wrong has not been resolved after almost thirty years of detailed study by some of the most talented minds in geophysics and petroleum engineering. The problem was a popular topic assigned to doctoral students in these disciplines [Wilkinson, 1960; Meeuwig, 1964; Haridasan, 1970; Jury, 1973; Okandan, 1974; Miller, 1983; Nimmo, 1983; Hopmans, 1985; Salehzadeh, 1990; She, 1997]. There have been numerous explanations for this disparity, all of which were based on reasonable suppositions about the nature of wetting liquids in porous media and all of which failed to give a completely satisfactory description of the phenomenon. Even though the phenomenon has not been resolved, much has been learned about porous media behavior. A great deal of this knowledge was due to failed attempts to understand the inadequacies of equation (3). In this Philip was wrong, but in being wrong, Philip opened up rich areas of study that has compelled geophysicists and engineers to explore the fundamentals of their understanding of natural phenomena.

The balance of this paper will present a selective survey of the experimental data describing the effect of temperature on capillary pressure. The paper will then review the explanations proposed to explain the phenomenon and suggestions for future research.

2. THE PHENOMENON

As far as we can determine, the effect of temperature on capillary pressure was first observed with a recording tensiometer by *Richards and Neal* [1937]. They acquired capillary pressure continuously in the field with a simple circular chart recorder, the design of which is presented in Figure 1. The circular chart, presented in Figure 2, showed that capillary pressures declined in the morning, as the soil warmed. The decrease in capillary pressure was most pronounced for tensiometer cups near the surface. While some of the phenomenon could have been due to the thermal expansion of liquids in the apparatus, their results indicated that capillary pressure decreased with increasing soil temperature.

Subsequently, the effect of temperature on capillary pressure was carefully studied in several laboratory studies. These studies generally, but not exclusively, consisted of determinations of capillary pressure satura-

Figure 1

Figure 2

tion relations determined at more than one temperature. Figure 3 presents an example of data collected in these studies, which indicated that temperature was having an effect, though because the capillary pressure saturation relations were themselves so complex, it was difficult to grasp the nature of the effect.

Figure 3

In comparison, *Gardner* [1955] plotted capillary pressures of a soil sample maintained at a constant degree of saturation as it was heated and cooled. This plot is presented here as Figure 4. Due to its simplicity, Figure 4 demonstrates clearly and convincingly the nature of the temperature effect, which was obscured by the complexity of Figure 3, that p_c decreases linearly with temperature. The data of *Gardner* [1955] suggest that capillary pressure at a particular temperature is not precisely reproducible after cycles of heating and cooling. *Faybishenko* [1983] conducted a study similar to *Gardner* [1955], but, as presented in Figure 5, found that capillary pressures at his observational temperatures were reproducible on cycles of heating and cooling and appeared to be linear functions of temperature. The results of *Gardner* [1955] and *Faybishenko* [1983] suggested that the effect of temperature on capillary pressure could be described by:

Figure 4

Figure 5

$$p_c = a_{p_c} + b_{p_c}T \quad (4)$$

where a_{p_c} and b_{p_c} are empirical constants (in pascals and pascals per kelvin, respectively).

As with capillary pressure, all known liquid-gas interfacial tensions are well described as linearly decreasing functions of temperature. Figure 6 presents the liquid-gas interfacial tensions of selected liquids from the comprehensive compilation of *Jasper* [1972]. We may write, therefore, the liquid-gas interfacial tensions as a similar linear function of temperature:

Figure 6

$$\gamma^{lg} = a_{\gamma^{lg}} + b_{\gamma^{lg}}T \quad (5)$$

where $a_{\gamma^{lg}}$ and $b_{\gamma^{lg}}$ are empirical constants (in newtons per meter and newtons per meter-kelvin, respectively). To facilitate the comparison of liquid-gas interfacial tensions of disparate liquids, equation (5) can be normalized by dividing through by its temperature derivative:

$$\frac{\gamma^{lg}}{\left(\frac{d\gamma^{lg}}{dT}\right)} = \frac{a_{\gamma^{lg}}}{b_{\gamma^{lg}}} + T. \quad (6)$$

We note here, and will return to, the fact that $a_{\gamma^{lg}}/b_{\gamma^{lg}}$ for pure water was equal to -766.45 K. Figure 7 replots the liquid-gas interfacial tension data presented in Figure 6 in terms of equation (6). Each line in Figure 7 had

Figure 7

a slope of 1 and an intercept equal to $a_{\gamma^{lg}}/b_{\gamma^{lg}}$. Following this example, equation (4) can be normalized by:

$$\frac{p_c}{\left(\frac{dp_c}{dT}\right)} = \frac{a_{p_c}}{b_{p_c}} + T. \quad (7)$$

Figure 8 presents a plot for capillary pressures of selected porous media similar to that in Figure 7. The dashed line in Figure 8 presents the line described by equation (6), that is, the expected relation if the temperature sensitivity of capillary pressure were due exclusively to the temperature-induced changes in the interfacial tension of pure water. As in Figure 7, the slope of each line is unity, and their intercepts are equal to a_{p_c}/b_{p_c} . Figure 8 made clear that capillary pressure was a linear function of temperature, that the phenomenon differed from porous medium to porous medium, and that for most soils, the relative change in capillary pressure with temperature was very different from that of the liquid-gas interfacial tension.

In a wholly different theoretical treatment, *Grant and Salehzadeh* [1996] assigned the variable name β_0 to the ratio a_{p_c}/b_{p_c} . Equation (7) can be integrated to yield:

$$p_{c(T=T_f)} = p_{c(T=T_r)} \left(\frac{\beta_0 + T_f}{\beta_0 + T_r} \right). \quad (8)$$

where T_r and T_f were the reference and observational temperatures (both in kelvins), respectively.

Subsequently, *Grant* [in press] estimated β_0 by nonlinear regression analysis for virtually all available water-air capillary pressure saturation relations measured at more than one temperature. His results were summarized in Table 1. He found that β_0 has values between -800 to -330 K, though generally far from -766 K. *Bachmann et al.* [in review] found that β_0 could be estimated well also from equation (7) and from transient flow experiments. *She and Sleep* [1998] found that equation (8) described well the capillary pressure saturation relations behavior of both water-air and water-tetrachloroethylene systems.

The preponderance of the studies conducted thus far have indicated that β_0 was largely unaffected by the degree of saturation. *Grant and Salehzadeh* [1996] found that the residuals of their nonlinear fits did not show a pronounced trend at the upper or lower extremes of the soils they studied. Similarly, *Bachmann et al.* [in review], who determined β_0 by calculating equation (7), found that β_0 was a weak linear function of water content.

There is an old joke that goes something like this:

First person: My uncle thinks he is a chicken.

Figure 8

Table 1

Second person: Why don't you take him to a psychiatrist?

First person: Because we need the eggs.

Equation (8) describes well the effect of temperature on capillary pressure, but the studies thus far have been unable to reconcile clearly equation (8) with any physical insight about capillary pressure in porous media. The following section reviews some of these attempts.

3. EXPLANATIONS OF THE PHENOMENON AND THEIR FAILURES

Three models have been developed to describe the enhanced sensitivity of capillary pressure to temperature, entrapped air, solutes, and temperature-sensitive contact angles. While the three will be discussed below, we begin with a digression to discuss the notion that the thermal expansion of water as a mechanism. It is likely that this mechanism was considered first, but never published because of its limitations. But it is a useful stage to begin this discussion since it illustrates the limitations of approaches based on the thermal expansion of the wetting liquid.

3.1. Water Expansion

While we know of no published works speculating on it, the first natural suggested mechanism to explain the discrepancy between the relative sensitivities of capillary pressure and surface tension of water would be due to the thermal expansion of water. If it is assumed that capillary pressure is solely a function of volumetric water content and surface tension, the total derivative of capillary pressure with respect to temperature becomes:

$$\frac{dp_c}{dT} = \frac{\partial p_c}{\partial \theta} \frac{\partial \theta}{\partial T} + \frac{\partial p_c}{\partial \gamma^{ls}} \frac{\partial \gamma^{ls}}{\partial T}. \quad (9)$$

The $\partial p_c / \partial \theta$ term in equation (9) reveals the greatest difficulty with models of capillary pressure temperature sensitivity based on thermal expansion of the liquid or gas entrapped in it. $\partial p_c / \partial \theta$ is a highly nonlinear function of θ . (Or, if it is inverted, $\partial \theta / \partial p_c$ is a highly nonlinear function of p_c .) Figure 9 presents $dp_c / d\theta$ as a function of capillary pressure for the sand studied by *She and Sleep* [1998]. It is unrealistic to assume that any function multiplied by (or divided by) $dp_c / d\theta$ will be linear or nearly linear. Accordingly, realistic models based on thermal expansion are unlikely.

Unfortunately for the proponents of these mechanisms, the preponderance of available evidence has indicated that the temperature sensitivity of capillary pressure is, at best, a weak function of water content.

Figure 9

Equation (9) could be divided through by p_c to yield, after rearrangement:

$$\frac{1}{p_c} \frac{dp_c}{dT} = \frac{1}{p_c} \frac{\theta}{1} \frac{1}{\frac{\partial \theta}{\partial p_c}} \frac{1}{\theta} \frac{\partial \theta}{\partial T} + \frac{1}{\gamma^{\text{ls}}} \frac{\partial \gamma^{\text{ls}}}{\partial T}. \quad (10)$$

If it is assumed further that the relation between capillary pressure and water content is described by the equation of *van Genuchten* [1980]

$$\theta = \theta_r + (\theta_s - \theta_r) \left\{ \frac{1}{[\alpha p_{c(T=T_r)}]^n + 1} \right\}^{\frac{n-1}{n}} \quad (11)$$

where α (in reciprocal pascals) and n (dimensionless) are empirical parameters; θ is volumetric water content (in cubic meters of water per cubic meter of soil); and θ_s and θ_r are the saturated and residual volumetric water contents (in cubic meters of water per cubic meter of soil), the three elements of equation (10) become:

$$\frac{1}{p_c} \frac{dp_c}{dT} = \frac{1}{\beta_0 + T} \quad (12)$$

$$\frac{1}{\gamma^{\text{lg}}} \frac{\partial \gamma^{\text{lg}}}{\partial T} = \frac{1}{\frac{a_{\gamma^{\text{lg}}}}{b_{\gamma^{\text{lg}}}} + T}, \quad (13)$$

and

$$\frac{1}{p_c} \frac{\theta}{1} \frac{1}{\frac{\partial \theta}{\partial p_c}} \frac{1}{\theta} \frac{\partial \theta}{\partial T} = \frac{[1 + (p_c \alpha)^n] \alpha_V \left\{ \left[\left(\frac{1}{1 + (\alpha p_c)^n} - 1 \right)^{\frac{1}{n} - 1} \right] \theta_r + \theta_s \right\}}{(n-1) (\alpha p_c)^n (\theta_r - \theta_s)} \quad (14)$$

where α_V (in reciprocal kelvins) is the volumetric coefficient of thermal expansion of water. At 298 K α_V has a value of 0.00026078 K⁻¹. Figure 10 presents these three elements of equation (10) for imbibition of an Elkmound sandy loam. The dark horizontal line approximates the relative effect of temperature on capillary pressure for this soil. The stippled horizontal line shows the relative effect of temperature on the surface tension of pure water. The dashed line shows the value of equation (14) for this soil. For this soil, the volumetric model was able to explain part of the observed discrepancy for some of the curves. The predictions of this model are not credible at the lower and higher extremes of capillary pressure.

Figure 10

3.2. Trapped Air Bubbles

A.J. Peck, a colleague of Philip's, suggested that trapped air was responsible for the enhanced sensitivity to temperature of capillary pressure [Peck, 1960].

This model and its successors [e.g., Chahal, 1964, 1995] suffer from the limitation of all models based on thermal expansion. Further, the central assumption of these models, that the volume of entrapped air increased with temperature, have not been supported by experiment.

Peck [1960] defined an apparent water volume as the sum of a “true” water volume and air bubbles trapped in the water that have no route to the external atmosphere:

$$\theta_{\text{H}_2\text{O(l),app}} = \theta_{\text{H}_2\text{O(l)}} + \theta_{\text{g,bub}} \quad (15)$$

where $\theta_{\text{H}_2\text{O(l),app}}$ was the apparent volumetric liquid water content (in cubic meters per cubic meter); $\theta_{\text{H}_2\text{O(l)}}$, volumetric liquid water content (in cubic meters per cubic meter); and $\theta_{\text{g,bub}}$, volumetric gas content in bubbles (in cubic meters per cubic meter). *Peck* [1960] assumed that the total differential of capillary pressure with respect to temperature was due to interfacial and volumetric effects

$$\begin{aligned} \frac{dp_c}{dT} = & \frac{\partial p_c}{\partial \theta_{\text{H}_2\text{O(l),app}}} \frac{\partial \theta_{\text{H}_2\text{O(l),app}}}{\partial T} \\ & + \frac{p_c}{\gamma^{\text{lg}}} \frac{\partial \gamma^{\text{lg}}}{\partial T}. \end{aligned} \quad (16)$$

Hopmans and Dane [1986b] carefully measured the volume of entrapped air in unsaturated soil columns at two temperatures and found that its volume actually decreased with temperature. A plausible explanation for this behavior was that it was due to the aqueous solubilities of gases, which decreased with increasing temperature [*Fogg and Gerrard*, 1990].

To make the problem more tractable, *Peck* [1960] assumed that the trapped air is composed of spherical bubbles with uniform radii. The pressure experienced by water in the porous matrix can be calculated by capillary pressure or by the radius of the bubbles:

$$p_{\text{g,bub}} - \frac{2\gamma^{\text{lg}}}{r_{\text{bub}}} = p_{\text{g}} - p_c \quad (17)$$

where $p_{\text{g,bub}}$ was pressure in gas bubbles (in pascals); p_{g} , pressure in the external gas phase (in pascals); and r_{bub} , radius of trapped bubble (in meters). The volume of \bar{N}_{bub} uniformly sized spherical bubbles in the unit volume of the porous matrix was

$$\theta_{\text{g,bub}} = \bar{N}_{\text{bub}} V_{\text{g,bub}} = \frac{4\pi r_{\text{bub}}^3 \bar{N}_{\text{bub}}}{3} \quad (18)$$

where \bar{N}_{bub} was number of bubbles per unit volume (in units per cubic meter) and V_{bub} , volume of a single bubble (in cubic meters). Since the pressure within a bubble and its volume were related by the gas law:

$$p_{\text{g,bub}} V_{\text{g,bub}} = n_{\text{g,bub}} RT \quad (19)$$

where R is the universal gas constant (in joules per kelvin-mole) and $\bar{n}_{g,bub}$, amount of gas trapped in bubbles per unit area (moles per cubic meter). Combining equations (17) and (19) yields

$$V_{g,bub} \left[p_g - p_c + 2\gamma^{lg} \left(\frac{4\pi\bar{N}_{bub}}{3V_{g,bub}} \right)^{1/3} \right] = n_{g,bub} RT. \quad (20)$$

Peck [1960] arrived at the following approximation:

$$\begin{aligned} \frac{dp_c}{dT} \approx & \frac{p_c}{\gamma^{lg}} \frac{\partial \gamma^{lg}}{\partial T} \\ & + \frac{\alpha_V \theta_{H_2O(l)} T (p_g - p_c)}{T(p_g - p_c) \partial \theta / \partial p_c - V_{g,bub}} \\ & + \frac{V_{g,bub} (p_g - p_c) - T \frac{p_c}{\gamma^{lg}} \frac{\partial \gamma^{lg}}{\partial T}}{T(p_g - p_c) \partial \theta / \partial p_c - V_{g,bub}}. \end{aligned} \quad (21)$$

From equation (7), it was known empirically that temperature sensitivity of capillary pressure for most soils was described well by:

$$\frac{dp_c}{dT} = \frac{p_c}{\beta_0 + T}. \quad (22)$$

Accordingly, the equation

$$\begin{aligned} \frac{p_c}{\beta_0 + T} \approx & \frac{p_c}{\gamma^{lg}} \frac{\partial \gamma^{lg}}{\partial T} \\ & + \frac{\alpha_V \theta_{H_2O(l)} T (p_g - p_c)}{T(p_g - p_c) \partial \theta / \partial p_c - V_{g,bub}} \\ & + \frac{V_{g,bub} (p_g - p_c) - T \frac{p_c}{\gamma^{lg}} \frac{\partial \gamma^{lg}}{\partial T}}{T(p_g - p_c) \partial \theta / \partial p_c - V_{g,bub}} \end{aligned} \quad (23)$$

could be solved for $V_{g,bub}$ as a function of capillary pressure. This was done for the soil parameters for drainage from a Plano silt loam (drainage) as estimated by *Grant and Salehzadeh* [1996]. Figure 11 presents the $V_{g,bub}$ so estimated.

Figure 11

The model of *Peck* [1960] must call upon widely varying and even negative values of entrapped air to describe the empirically described effect of temperature on capillary pressure. To be fair, these negative values of entrapped air may be due to the simplifying assumption of spherical bubbles. Negative bubbles may be calculated because the phenomenon is due to the expansion of entrapped air at pore throats, whose behavior is poorly represented by spherical bubbles. Subsequent researchers have found the model of *Peck* [1960] successful.

3.3. Solutes

Soil solutions are typically dilute (ca. $0.01 \text{ mol} \cdot \text{kg}^{-1}$) aqueous solutions with a variety of inorganic and organic solutes. Since it is well known that solutes can

have a pronounced effect on the thermophysical properties of the solution, it is reasonable to expect that the unexpectedly large effect of temperature capillary pressure may be due to the influence of solutes. Additionally, natural organic solutes sorb to mineral surfaces to form “conditioning films” with surface properties different from those of the pristine mineral surface [Schneider, 1996]

For water to spread on a surface, the adhesive forces must exceed the cohesive forces within the bulk water. A contact angle of 90° arises when the solid surface tension is $\gamma^{lg}/4$; a zero contact angle occurs when the surface tensions of solid and liquid are equal [Letey *et al.*, 2000]. If the interfacial tension of the solid is smaller than the surface tension of pure liquid water, solutes in the soil solution may have a considerable impact on the contact angle. Increasing interfacial tension between the liquid and gas phases γ^{lg} may lead to greater contact angles, and a reduction of the liquid interfacial tension may decrease the contact angle. We are aware of only one study that found that the surface tension of soil solution was higher than for pure water. Hartge [1958] showed that liming his soils under study increased the concentration of inorganic cations in the solution, which increased the liquid surface tension to values around $76 \text{ mN}\bullet\text{m}^{-1}$ at 20°C . More often, a reduction of the liquid interfacial tension was observed. The presence of both hydrophilic polar and hydrophobic structural units of natural organic compounds can be expected to promote accumulation at the liquid-gas interface, which thereby influences the solution surface tension [Anderson *et al.*, 1995]. Humic and fulvic acids, proteins, fatty acids, and other organic compounds of natural ecosystems possess both hydrophobic (aromatic rings and aliphatic hydrocarbons) and hydrophilic (oxygen-containing) functional groups. This suggests that, like synthetic surfactants, these compounds would exhibit significant surface activity. Chen and Schnitzer [1978] demonstrated that pyrolyzed fulvic acid, which had lost the functional groups, lowered the surface tension of water only slightly. The potential of humic and fulvic acids to lower the soil surface tension was shown by Chen and Schnitzer [1978]. For humic acid dissolved in water, a linear reduction to values of $43 \text{ mN}\bullet\text{m}^{-1}$ and for fulvic acid a hyperbolic decrease to values of $44 \text{ mN}\bullet\text{m}^{-1}$ were observed, whereas Tschapek *et al.* [1978] observed only a decrease in surface tension of diluted soil solutions of about $9 \text{ mN}\bullet\text{m}^{-1}$. Temperature may have a significant effect on the solubility of surfactants in the soil solution. As reported by Nimmo and Miller [1986], the temperature effect on the surface tension of soil solu-

tions is larger than for pure water. Unfortunately most of the measurements of the interfacial tension of soil solution were made without considering the temperature effect. It was shown that the solubility of fatty acids may increase with temperature by a factor of 2 to 3 for a temperature increase from 0 to 60 °C [Singleton, 1960, cited by Nimmo and Miller, 1986]. Chen and Schnitzer [1978] showed further that lipid-enriched leaf extracts of poplar and maple decreased the surface tension of water of 72 mN•m⁻¹ effectively by 30 %. Anderson *et al.* [1995] demonstrated that humic acid-water solutions decrease linearly in surface tension with increasing concentration. The temperature had a substantial effect on the liquid interfacial tension. Surface tension reductions were linear with increasing temperature. Surface tension reductions per kelvin were found to be twice as high compared with pure water of -0.138 mN•m⁻¹•K⁻¹.

3.4. Contact angles

3.4.1. *The nonzero contact angle phenomenon in soils.* The cosine of the contact angle at the intersection of the gas, liquid, and solid phases is related to the pertinent interfacial tensions by

$$\cos \Theta = \frac{\gamma^{ls} - \gamma^{gs}}{\gamma^{lg}} \quad (24)$$

where γ^{ls} and γ^{gs} are the liquid-solid and gas-solid interfacial tensions (in newtons per meter), respectively [Rowlinson and Widom, 1982]. In order to discuss the wetting coefficient as a relevant factor affecting the temperature dependence of the capillary pressure, it is essential to realize that, in general, porous media exhibit nonzero contact angles with respect to water or soil solution. This statement should not be considered trivial, because in the past most scholars assumed complete wetting, except the few who focussed on eye-catching “extremely water repellent” soils [Doerr *et al.*, 2000]. Until now, only a few studies indicate that, besides water repellency, “all other soils” or packings of glass beads [Lu *et al.*, 1994] were interacting with the soil solution or water with nonzero contact angles.

Langmuir reported in 1919 in a lecture to the Faraday Society that an adsorbed monolayer of some organic compound could radically change the frictional and wetting properties of the solid surface [Zisman, 1964]. Selective sorption of organic molecules, as it was observed for aliphatic alcohol from water to silica surfaces [Tschapek, 1984], or the loss of water through evaporation, allows the deposition of solutes on the surface of the mineral.

Surface tensions of hard solids, like metals and minerals, range from $5000 \text{ mN}\cdot\text{m}^{-1}$ (high-energy surfaces), depending on their hardness and melting point, down to $9 \text{ mN}\cdot\text{m}^{-1}$ for closed packed $-\text{CF}_3$ groups [Zisman, 1964]. Soft organic solids have much lower melting points, and the surface tension is generally less than $100 \text{ mN}\cdot\text{m}^{-1}$. The few measurements of interfacial tension in soil [Miyamoto and Letey, 1971] indicate small values. These authors reported interfacial tensions for quartz sand of about $43 \text{ mN}\cdot\text{m}^{-1}$, for water-repellent soil of $25 \text{ mN}\cdot\text{m}^{-1}$, and for silane-treated soil around $10 \text{ mN}\cdot\text{m}^{-1}$. It has also been argued that all the inorganic soil minerals were hydrophilic because their surfaces usually hold ions and polar groups [Tschapek, 1984]. The hydrophilicity of minerals increases together with the densities of their surface charges and surficial polar groups.

Generally, a hydrophobic surface in contact with water can remain hydrophobic, as long as the interaction between water and a hydrophobic surface takes place through dispersive forces, while the polar forces remain free. According to the comprehensive review article by Doerr *et al.* [2000], the breakdown of hydrophobicity can be caused by the migration of surface-active substances in contact with water. The combination of surface properties and topology of the porous media emphasizes that observations were, at best, apparent contact angles, which cannot be related directly to the contact angle at interfaces within the medium [Philip, 1971].

When in studies about the temperature dependence of the contact angle, apparent contact angles were determined through capillary ascent, the tendency was a decrease of the contact angle with increasing temperature [King, 1981]. The soils studied by King [1981] had contact angles between 75 and 99° and were rated from not water repellent to severely water repellent. It was also shown that the temperature dependence of all soils increased with increasing contact angle and that in all cases it was considerably larger than estimated for pure water. Over the temperature range 0 to 36°C , a negative linear relationship between capillary ascent and temperature was obtained. The height of water rise of the reference medium (ignited soil) was not affected by temperature. Further evidence for nonzero contact angles was provided by Siebold *et al.* [1997] with the capillary rise technique. For silica powder ($<123 \mu\text{m}$, $99.5\% \text{ SiO}_2$) and for limestone particles ($>460 \mu\text{m}$, $98\% \text{ CaCO}_3$), contact angles of 56° to 79° were measured. The above findings indicate that a wetting coefficient <1 (i.e., contact angles $> 0^\circ$) was not restricted to a

few hydrophobic soils. It seems that weathered mineral surfaces or coatings and hydrophobic particles in the pore space of wettable mineral particles reduced the wettability of the high-energy surfaces to values $< 72 \text{ mN}\bullet\text{m}^{-1}$. It was further interesting to note that according to *King* [1981], soils classified with the conventional Water Drop Penetration Time (WDPT) Test as soils with a low degree of water repellency (WDPT $< 60 \text{ s}$) have contact angles up to 86° .

Experiments conducted with wettable soils and their water-repellent counterparts having identical textures showed that the contact-angle decrease with temperature is between $-0.03^\circ\bullet\text{K}^{-1}$ and $-0.26^\circ\bullet\text{K}^{-1}$ [*Bachmann et al.*, 2001, Table 1]. These values agreed with those cited by *She and Sleep* [1998]. The results of *Bachmann et al.* [in review] suggested further that equation (16), which predicts an increase of the contact angle with increasing temperature, did not match the observed tendency to lower contact angles with increasing temperature in a partly saturated porous medium. However, Figure 12 shows contact angles measured with the sessile drop method for dry soil treated with different amounts of dimethyldimethylsilane. In this case, an increase of the contact angle with increasing temperature was found. The largest temperature effects were observed for the soil with contact angles around 90° at 20°C .

Figure 12

3.4.2. Interaction of capillary water and adsorbed water films. The adsorption of water vapor leads to a decrease of the interfacial tension between the solid and the gas. Bangham and Razouk [cited in *Schrader*, 1993] stated that "...the adsorbed vapor phase and bulk liquid in contact with the solid surface must be regarded as distinct thermodynamic entities, separated in general by a discontinuity." Although not stated directly, the derivation of equation (28) did not include explicitly the physical nature of the thin water films either already adsorbed on the solid surface or adsorbed as droplets or menisci. Taking the case that the vapor phase was replaced by the liquid, then the decrease of the interfacial tension was $\gamma^{\text{lg}} \cos \Theta$. The decrease of the interfacial tension taking place when water vapor was adsorbed was proportional to the temperature and the integral of the number of moles adsorbed per unit area at pressure p [*Schrader*, 1993]. An increase of water repellency with an increasing amount of water was phenomenologically observed for soils [see review paper *Doerr et al.*, 2000]. Most studies on the temperature effect on capillary pressure have been conducted for intermediate water contents. In this case it could be assumed that water films and menisci existed simultaneously. This

may have had important consequences for the contact angle of the solid-liquid interface. Under an initially dry condition, the wetting front proceeded like a jump behavior at the particle with the smallest diameter, while a very thin, unobservable water film may have existed on the surfaces. Under an initially wet condition, capillary rise occurred as a film thickening process [Lu *et al.*, 1994]. Derjaguin and Churaev [1986] suggested separating thin water films into two regions with different physical properties. It was assumed that thinner α -films are caused by structural forces and thicker β -films by electrostatic forces. The transition from an α - to a β -film is characterized by complete wetting (contact angle = 0°). It was found that the range of thickness of films varied between 3.0 and 27.0 nm. With an increasing contact angle, the film thickness decreased. This effect was observed on glass, quartz, and mica surfaces. Derjaguin and Churaev [1986] indicate also that an increasing temperature leads to thinner water films and increasing contact angles. The general behavior of a surface during adsorption of water vapor (drop formation or film formation) can be derived from water vapor adsorption isotherms [Schrader, 1993].

3.4.3. Temperature-sensitive contact angles. Grant and Salehzadeh [1996] explored the notion that the phenomenon was due to temperature-induced changes in the contact angle. If a temperature-sensitive contact angle is accepted conditionally, then the temperature derivative of equation (1) becomes

$$\frac{1}{p_c} \frac{dp_c}{dT} = \frac{1}{\gamma^{\text{lg}}} \frac{d\gamma^{\text{lg}}}{dT} + \frac{1}{\cos \Theta} \frac{d \cos \Theta}{dT}. \quad (25)$$

As discussed in Section 2, for pure water

$$\frac{1}{\gamma^{\text{lg}}} \frac{d\gamma^{\text{lg}}}{dT} = \frac{1}{\frac{a}{b} + T}. \quad (26)$$

It remains therefore to derive an expression for

$$\frac{1}{\cos \Theta} \frac{d \cos \Theta}{dT}. \quad (27)$$

Equation (27) can be evaluated with a frequently cited, but rarely tested, expression first derived by Harkins and Jura [1944]:

$$-\Delta_{\text{sg}}^{\text{sl}} h^{\text{s}} = \gamma^{\text{lg}} \cos \Theta - T \frac{d(\gamma^{\text{lg}} \cos \Theta)}{dT} \quad (28)$$

where $-\Delta_{\text{sg}}^{\text{sl}} h^{\text{s}}$ is the enthalpy of immersion per unit area (in joules per square meter).

If it is assumed that

$$\frac{d\Delta_{\text{sg}}^{\text{sl}} h^{\text{s}}}{dT} = 0$$

one derives immediately

$$\cos \Theta = \frac{-\Delta_{sg}^{sl} h^s + T \mathbf{C}_1}{a + bT} \quad (29)$$

where \mathbf{C}_1 is a constant of integration. Equation (25) can then be evaluated directly:

$$\frac{1}{p_c} \frac{dp_c}{dT} = \frac{1}{\beta_0 + T} \quad (30)$$

where

$$\beta_0 = \frac{-\Delta_{sg}^{sl} h^s}{\mathbf{C}_1}. \quad (31)$$

Substituting equations (30) and (26) into equation (25) yields:

$$\frac{1}{\beta_0 + 1} = \frac{1}{\frac{a}{b} + 1} + \frac{1}{\cos \Theta} \frac{d \cos \Theta}{dT}. \quad (32)$$

Clearly, if $d \cos \Theta / dT = 0$, as assumed implicitly by *Philip and de Vries* [1957], then $\beta_0 = a/b = -766.45$ K.

Equation (8) can be derived from first principles and describes virtually all available capillary pressure saturation relation data well. In spite of this, *She and Sleep* [1998] found a serious problem with equation (30). For consistency we are presenting their argument more in keeping with the treatment in this article. We hope they agree that this treatment reflects their ideas.

While there is a not inconsiderable uncertainty in the measurements, the available data indicate that the contact angle in soils is generally in a wide range between 0° and $> 90^\circ$ and that the contact angle is a decreasing function of temperature.

Rearrangement and simplification of equation (32) yields

$$\tan \Theta \frac{d\Theta}{dT} = \frac{180}{\pi} \left(\frac{1}{\frac{a}{b} + T} - \frac{1}{\beta_0 + T} \right). \quad (33)$$

Equation (33) demonstrates the perils of formulating this wettability of porous media in terms of contact angles. The graph of the function $\tan \Theta$ has a discontinuity at 90° , $\lim_{\Theta \rightarrow 90^\circ} \tan \Theta = +\infty$ when approached from below 90° and $-\infty$ when approached from above. Since at 298 K

$$\frac{1}{\frac{a}{b} + T} = -0.002145$$

and at the same temperature the average value of β_0 for the soils studied thus far yields

$$\frac{1}{\beta_0 + T} = -0.00844,$$

it would be expected that

$$\tan \Theta \frac{d\Theta}{dT} \approx 0.36. \quad (34)$$

For virtually all soils studied the right hand side of equation (34) is positive. This implies that $\tan \Theta$ and $\frac{d\Theta}{dT}$ must have the same sign. Assuming that $d\Theta/dT < 0$ and recalling that $\tan \Theta > 0$ for $0^\circ < \Theta < 90^\circ$ and $\tan \Theta < 0$ for $90^\circ < \Theta < 180^\circ$, equation (34) will hold only for $\Theta < 90^\circ$, which is inconsistent with the “conventional wisdom” about the wettability of natural porous media.

4. CONCLUDING REMARKS

The effect of temperature on capillary pressure is a linearly decreasing function of temperature well described by equation (8). The parameter β_0 appears to be unaffected or weakly affected by water content. It is unlikely that a mechanism due to the thermal expansion of the soil solution or its constituents can describe the effect of temperature on capillary pressure. The most likely mechanisms are solute effects on the soil solution surface tension or temperature-induced changes in contact angles.

It is important to note that the general belief that soils exhibit nonzero contact angles may be invalid. Generally, the wetting coefficient may be one of three candidate mechanisms for the larger-than-expected temperature-dependence of the capillary pressure. In our opinion, wetting coefficients are temperature dependent. However, although the temperature effect is clearly observable for sessile drops on relatively dry soil particles, there are very few studies conducted to investigate the temperature effect on the contact angle of surfaces in contact with water. Generally, a larger temperature factor β_0 in equation (8) results in lower capillary forces at high temperatures because increasing temperature affects the capillary pressure in the same direction (to less negative values) as an increasing contact angle. This effect, however, cannot be quantified without additional measurements of the temperature dependence of the soil solution surface tension.

Further important research gaps can be identified. Soils are generally structured. However, no attempt has been made to investigate the wetting coefficient of outer and inner aggregate surfaces. Even when some experiments made on water/glass-bead systems indicate that solutes do not cause a temperature dependence, alternative methods of investigation (e.g., the calorimetric method) seem to confirm the assumption of a temperature dependence of the wetting coefficient according to equation (28).

Resolution of these issues will require novel experimental techniques and new physical insights. Forty-four years after its publication, the questions raised by *Philip and de Vries* [1957] continue to compel the geophysics community to the limits of understanding.

NOTATION

a_{p_c}	fitted parameter, Pa
$a_{\gamma^{ls}}$	fitted parameter, N/m
b_{p_c}	fitted parameter, Pa/K
$b_{\gamma^{ls}}$	fitted parameter, N/(m K)
n	van Genuchten equation parameter, dimension 1
$\bar{n}_{g,bub}$	amount of gas trapped in bubbles per unit area mol/m ³
\bar{N}_{bub}	number of bubbles per unit volume, m ⁻³
p_c	capillary pressure, Pa
p_g	pressure in the external gas phase, Pa
$p_{g,bub}$	pressure in gas bubbles, Pa
r	pore radius, m
r_{bub}	radius of trapped bubble, m
R	universal gas constant, J/(K mol)
$s^{s,\alpha\beta}$	interfacial entropy per unit area between α and β phases, J/(K m ²)
V_{bub}	volume of a single bubble, m ³
T	temperature, K
T_f	observational temperature, K
T_r	reference temperature, K
α	van Genuchten equation parameter, Pa ⁻¹
α_V	the cubic expansion coefficient of water, K ⁻¹
β_0	parameter, K
γ^{lg}	interfacial tension between the liquid and gas phases, N/m
γ^{ls}	interfacial tension between the liquid and solid phases, N/m
γ^{sg}	interfacial tension between the solid and gas phases, N/m
θ	volumetric soil-water content, m ³ /m ³
$\theta_{g,bub}$	volumetric gas content in bubbles, m ³ /m ³
$\theta_{H_2O(l)}$	volumetric liquid water content, m ³ /m ³
$\theta_{H_2O(l),app}$	apparent volumetric liquid water content, m ³ /m ³
θ_r	residual volumetric soil-water content, m ³ /m ³
θ_s	saturated volumetric soil-water content, m ³ /m ³
Θ	contact angle of the liquid-gas interface with the solid, °

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REFERENCES

- Anderson, M.A., A.Y.C. Hung, D. Mills, and M.S. Scott, Factors affecting the surface tension of soil solutions and solutions of humic acids, *Soil Sci.*, 160, 111-116, 1995.
- Bachmann, J., Measurement and simulation of nonisothermal moisture movement in water-repellent mineral soils, *Z. Pflanzenernähr Bodenk.*, 161, 147-155, 1998 [In German].
- Bachmann, J., R. Horton, S.A. Grant, and R.R. van der Ploeg, Temperature dependence of soil water retention curves of wettable and water repellent soils, *Soil Sci. Soc. Am. J.*, [in press].
- Bachmann, J., R. Horton, R.R. van der Ploeg, and S.K. Woche, Modified sessile-drop method assessing initial soil water contact angle of sandy soil, *Soil Sci. Soc. Am. J.*, 64, 564-567, 2000.
- Chahal, R.S., Effect of temperature and trapped air on the energy status of water in porous media, *Soil Sci.*, 98, 107-112, 1964.
- Chahal, R.S., Effect of temperature and trapped air on matrix suction, *Soil Sci.*, 100, 262-266, 1965.
- Chen, Y., and M. Schnitzer, The surface tension of aqueous solutions of soil humic substances, *Soil Sci.*, 125, 7-15, 1978.
- Constantz, J., Temperature dependence of unsaturated hydraulic conductivity of two soils, *Soil Sci. Soc. Am. J.*, 46, 466-470, 1982.
- Constantz, J., Laboratory analysis of water retention in unsaturated zone materials at high temperature, pp. 147-164, in J. W. Mercer, P.S.C. Rao, and I. W. Marine, eds., *Role of the Unsaturated Zone in Radioactive and Hazardous Waste Disposal*, Ann Arbor, Michigan, Ann Arbor Press, 1983.
- Constantz, J., Comparison of isothermal and isobaric water retention paths in non-swelling porous materials, *Water Resour. Res.*, 27, 3165-3170, 1991.
- Crausse, P., Etude fondamentale des transferts couplés de chaleur et d'humidité en milieu poreux non saturé, 207 pp., Thèse d'Etat, Institut National Polytechnique de Toulouse (France), 1983.
- Doerr, S.H., R.A. Shakesby, and R.P.D. Walsh, Soil water repellency: its causes, characteristics and hydro-geomorphological significance, *Earth Sci. Rev.*, 51, 33-65, 2000.
- Davis, E.L., Effect of temperature and pore size on the hydraulic properties and flow of a hydrocarbon oil in the subsurface, *J. Contam. Hydrol.*, 16, 55-86, 1994.
- Derjaguin, B.V. and N.V. Churaev, Properties of water layers adjacent to interfaces, pp. 663-738, in, C.A. Croxton, ed., *Fluid Interfacial Phenomena*, New York, Wiley, 1986.
- de Vries, D.A., The theory of heat and moisture transfer in porous media revisited, *Int. J. Heat Mass Transfer*, 30, 1343-1350, 1987.
- de Vries, D.A., and J.R. Philip, Soil heat flux, thermal conductivity, and the null-alignment method, *Soil Sci. Soc. Am. J.*, 50, 12-17, 1987.
- Faybishenko, B., Effect of temperature on moisture content, entropy, and water pressure in loam soils, *Pochvovedenie*, 12, 1983 [In Russian].

- Fogg, P.G.T., and W. Gerrard, *Solubility of Gases in Liquids*, New York, Wiley, 1991.
- Gardner, R., Relations of temperature to moisture tension of soil, *Soil Sci.*, 79, 257-265, 1955.
- Grant, S.A., Extension of a temperature-effects model for capillary-pressure saturation relations, *Water Resour. Res.*, 200- [in press].
- Grant, S.A. and A. Salehzadeh, Calculation of temperature effects on wetting coefficients of porous solids and their capillary pressure functions, *Water Resour. Res.*, 32, 261-270, 1996.
- Haridasan, M., Effect of temperature on pressure head-water content relationship and conductivity of two soils, Ph.D. dissertation, Mississippi State Univ., Starkville, *Diss. Abstr.* 32/07b:3740, 1970.
- Haridasan, M., and R.D. Jensen, Effect of temperature on pressure head-water content relationship and conductivity of two soils, *Soil Sci. Soc. Am. J.*, 36, 703-708, 1972.
- Harkins, W.D., and G. Jura, Surfaces of solids, 12., An absolute method for the determination of the area of a finely divided crystalline solid, *J. Am. Chem. Soc.*, 66, 1362-1366, 1944.
- Hartge, K.H., *Die Wirkung des Kalkes auf die Strukturstabilität von Ackerböden*, Dissertation, Department of Horticulture, Technical University of Hannover, Germany. 1958 [in German].
- Hopmans, W.J., Thermal effects on soil water transport, Ph.D. dissertation, Auburn Univ., Auburn, Alabama, *Diss. Abstr.* 46/08b:2507, 1985.
- Hopmans, J.W., and J.H. Dane, Temperature dependence of soil hydraulic properties, *Soil Sci. Soc. Am. J.*, 50, 4-9, 1986a.
- Hopmans, W.J., and J.H. Dane, Temperature dependence of soil water retention curves, *Soil Sci. Soc. Amer. J.*, 50, 562-567, 1986b.
- Jasper, J.J., Surface tension of pure liquid compounds, *J. Phys. Chem. Ref. Data*, 1, 841-1009, 1972.
- Jury, W.A., Simultaneous transport of heat and moisture through a medium sand, Ph.D. dissertation, Univ. Wisconsin, Madison, Dissertation Abstracts Vol. 34/08b:3585, 1973.
- King, P.M., Comparison of methods for measuring severity of water repellence of sandy soils and assessment of some factors that affect its measurement, *Aust. J. Soil Res.*, 19, 275-285, 1981.
- Letey, J., M.L.K. Carillo, and X.P. Pang, Approaches to characterize the degree of water repellency, *J. Hydrol.*, 231-232, 61-65, 2000.
- Lu, T.X., J. W. Biggar, and D.R. Nielsen, Water movement in glass beads porous media, 2., Experiments of infiltration and finger flow, *Water Resour. Res.*, 28, 3283-3290, 1994.
- Meeuwig, R.O., Effects of temperature on moisture conductivity in unsaturated soil, Ph.D. dissertation, Utah State Univ., Logan, *Diss. Abstr.* 25/06:3180, 1964.
- Miller, M.A., Laboratory evaluation of in situ steam flushing for NAPL removal from soil, Ph.D. dissertation, Stanford Univ., Stanford, California, *Diss. Abstr.* 44/05b:1568, 1983.
- Miyamoto, S. and J. Letey, Determination of solid-air surface tension of porous media, *Soil Sci. Soc. Amer. Proc.*, 35, 856-859, 1971.

- Novák, V., Non-isothermal flow of water in unsaturated soil, *J. Hydrol. Sci.*, 2, 37-52, 1975.
- Nimmo, J.R., The temperature dependence of soil-moisture characteristics, Ph.D. dissertation, Univ. Wisconsin, Madison, *Diss. Abstr.* 44/06b:1858, 1983.
- Nimmo, J.R., and E.E. Miller, The temperature dependence of isothermal moisture vs. potential characteristics of soils, *Soil Sci. Soc. Am. J.*, 50, 1105-1113, 1986.
- Okandan, E., The effect of temperature and fluid composition on oil-water capillary pressure curves of limestone and sandstones and measurement of contact angle at elevated temperatures, Ph.D. dissertation, Stanford Univ., Stanford, California, *Diss. Abstr.* 34/12b:6027, 1974.
- Peck, A.J., Change of moisture tension with temperature and air pressure, Theoretical, *Soil Sci.*, 89, 303-310, 1960.
- Philip, J.R., Limitations on scaling by contact angle, *Soil Sci. Soc. Amer. Proc.*, 35, 507-509, 1971.
- Philip, J.R., and D.A. de Vries, Moisture movement in porous materials under temperature gradients, *Trans. Amer. Geophys. Union*, 38, 222-232, 1957.
- Richards, L.A., and O.R. Neal, Some field observations with tensiometers, *Soil Sci. Soc. Am. Proc.*, 1, 71-91, 1937.
- Rowlinson, J.S., and B. Widom, *Molecular Theory of Capillarity*, Clarendon Press, Oxford, 1982.
- Salehzadeh, A., The temperature dependence of soil moisture characteristics of agricultural soils, Ph.D. dissertation, Univ. Wisconsin, Madison, *Diss. Abstr.* 51/09b:4245, 1990.
- Schneider, R.P., Conditioning film-induced modification of substratum physicochemistry, Analysis by contact angles, *J. Colloid Interface Sci.*, 182, 204-213, 1996.
- Schrader, M.E., Sessile drops, Do they really stand on solid surfaces? pp. 109-121, in, Mittal, K.L., ed., *Contact Angle, Wettability and Adhesion*, Utrecht, The Netherlands, VSP, 1993.
- She, H.Y., Laboratory evaluation of in situ steam flushing for NAPL removal from soil, Ph.D. dissertation, Univ. Toronto, *Diss. Abstr.* 59/06b:2918, 1997.
- She, H.Y., and B. Sleep, The effect of temperature on capillary pressure-saturation relationships for air-water and tetrachloroethylene-water systems, *Water Resour. Res.*, 34, 2587-2597, 1998.
- Siebold, A., A. Walliser, M. Nardin, M. Opplinger, and J. Schultz, Capillary rise for thermodynamic characterization of solid particle surface, *J. Colloid Interface Sci.*, 186, 60-70, 1997.
- Singleton, W.S., Solution properties, p. 609-682 in K. Marley, ed., *Fatty acids*, New York, Interscience, 1960.
- Taylor, S.A., The activity of water in soils, *Soil Sci.*, 86, 83-90, 1958.
- Tschapek, M., C.O. Scoppa, and C. Wasowski, The surface tension of soil water, *J. Soil Sci.*, 29, 17-21, 1978.
- Tschapek, M., Criteria for determining the hydrophilicity-hydrophobicity of soils, *Z. Pflanzenernähr Bodenk.*, 147, 137-149, 1984.
- van Genuchten, M.Th., A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.*, 44, 892-898, 1980.
- Wilkinson, G.E., The temperature effect on the equilibrium energy status of water held by porous media, Ph.D. dissertation, Univ. Illinois, Urbana-Champaign, *Diss. Abstr.* 21/10:2916, 1960.

Wilkinson, G.E. and A. Klute, The temperature effect on the equilibrium energy status of water held by porous media, *Soil Sci. Soc. Am. Proc.*, 26, 326-329, 1962.

Zisman, W.A., Relation of equilibrium contact angle to liquid and solid construction, in, Gould, R.F. (ed.), *Contact angle, wettability and adhesion*, Advan. in Chem., Series 43, 1-51, Washington, D.C., Amer. Chem. Soc., 1964.

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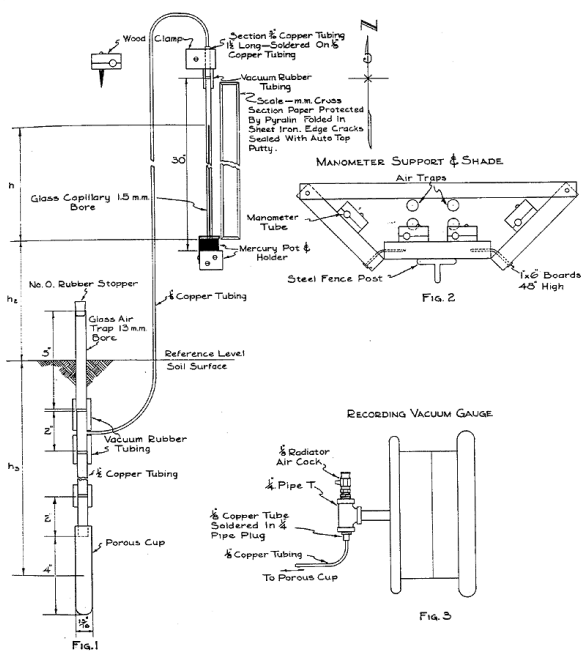


Figure 1. Schematic drawing of an early recording tensiometer described by *Richards and Neal* [1937].

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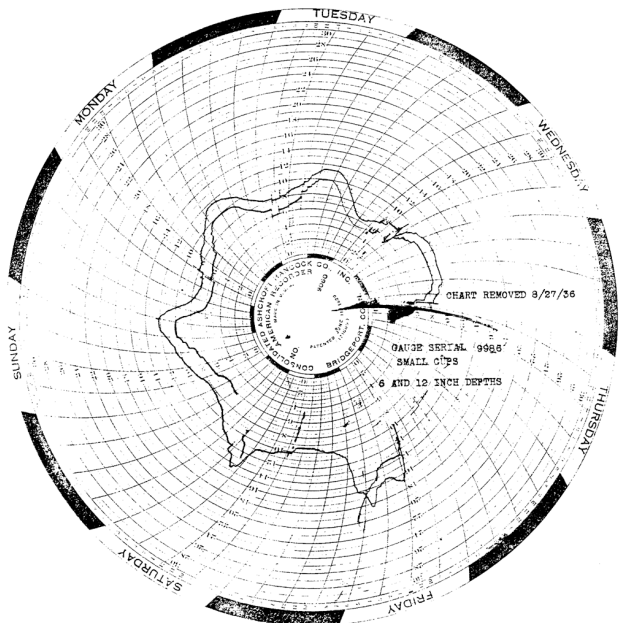


Figure 2. Capillary pressures recorded by *Richards and Neal* [1937] showing a daily decrease in capillary pressure in the morning as the soil warmed.

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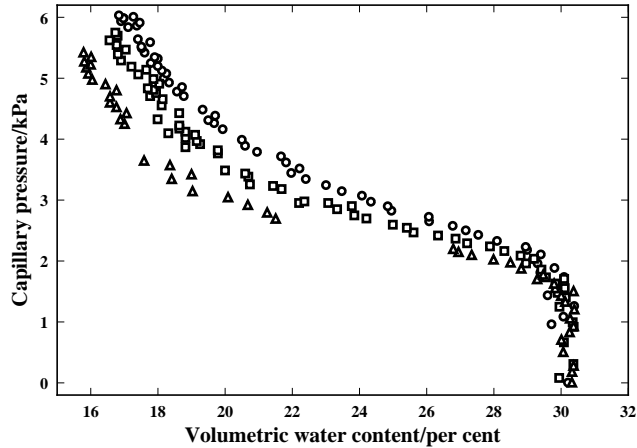


Figure 3. Capillary pressure saturation relations of a Plainfield sandy loam soil measured at 19.1 (circles), 34.1 (squares), and 49.2 °C (triangles) as reported by *Nimmo and Miller* [1986].

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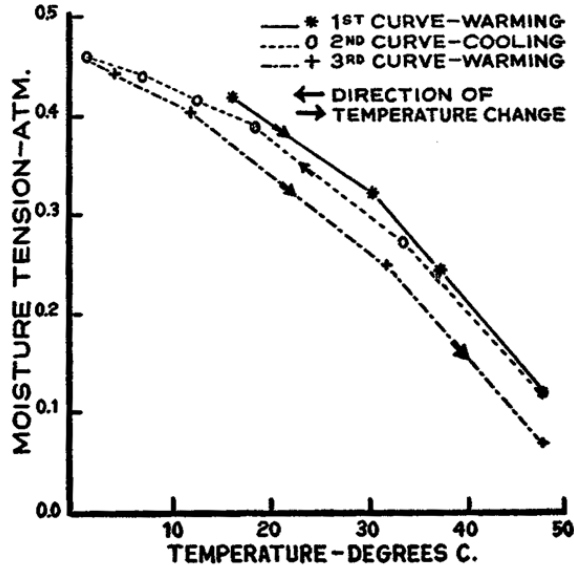


Figure 4. Capillary pressures presented by *Gardner* [1955] of a coarse sand at 2.2 % water content subjected to heating and cooling cycles.

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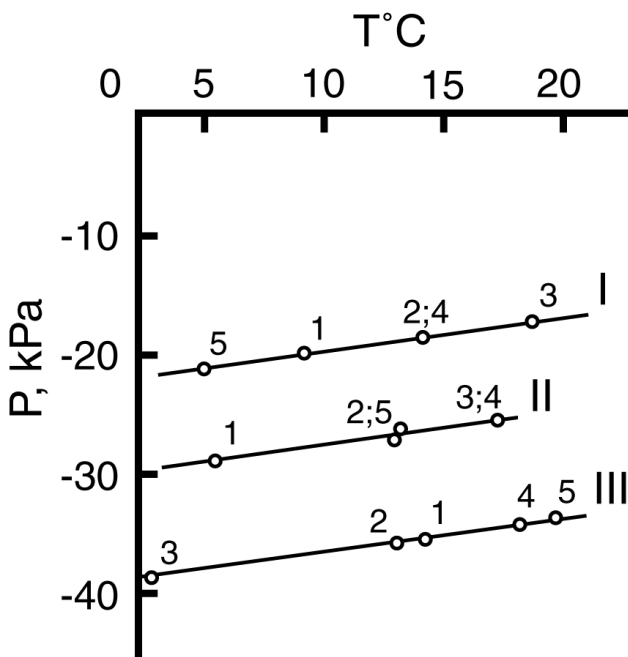


Figure 5. Capillary pressure measured by *Faybishenko* [1983] on a loam soil at three constant water contents, but at a range of temperatures. Roman numerals refer to water contents (I: 0.347 m³•m⁻³, II: 0.326 m³•m⁻³, III: 0.3 m³•m⁻³). Arabic numbers refer to steps in heating-and-cooling cycles.

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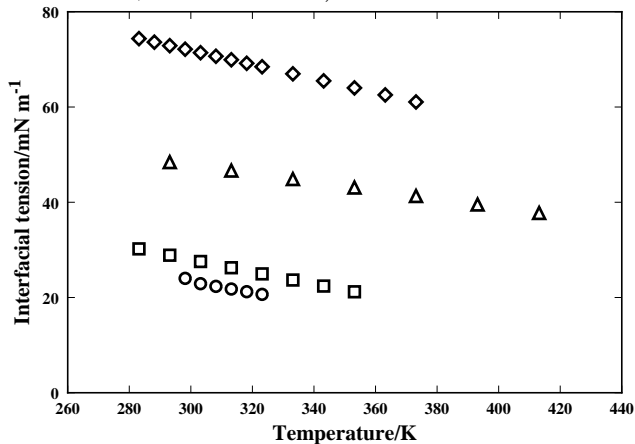


Figure 6. Liquid-gas interfacial tensions of selected liquids at a range of temperatures: acetone (circles), benzene (squares), ethylene glycol (triangles), and water (diamonds).

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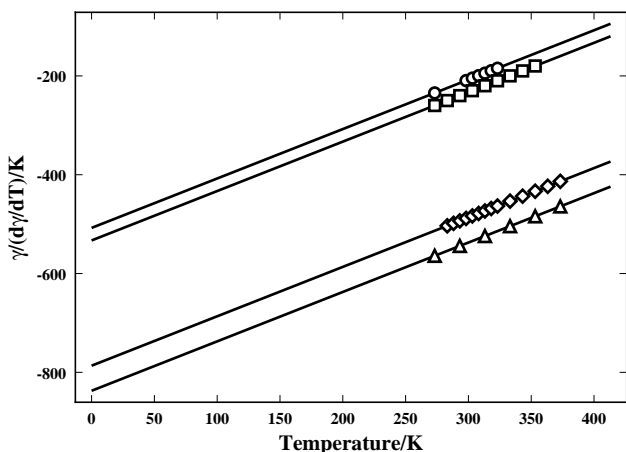


Figure 7. Normalized values of liquid-gas interfacial tensions as functions of temperature: acetone (circles), benzene (squares), ethylene glycol (triangles), and water (diamonds).

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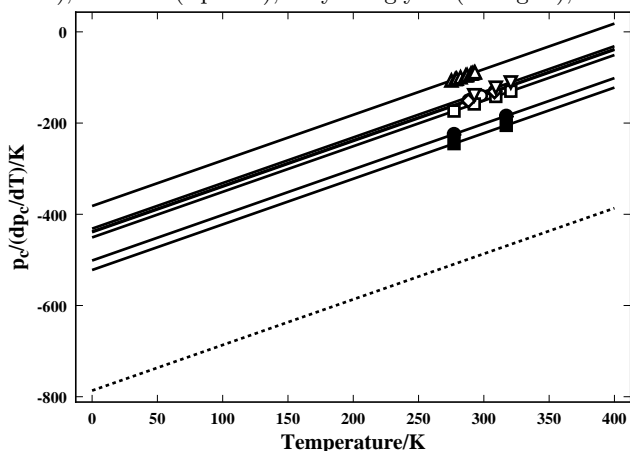


Figure 8. Normalized values of capillary pressure of selected porous media measured at different temperatures: Dubbs silt loam (circles), glass beads (squares), loam (upright triangles), Norfolk sandy loam (diamonds), Plainfield sand (inverted triangles), sand (filled circles), and silt (filled squares). The dashed line is the expected normalized value for the surface tension of pure water.

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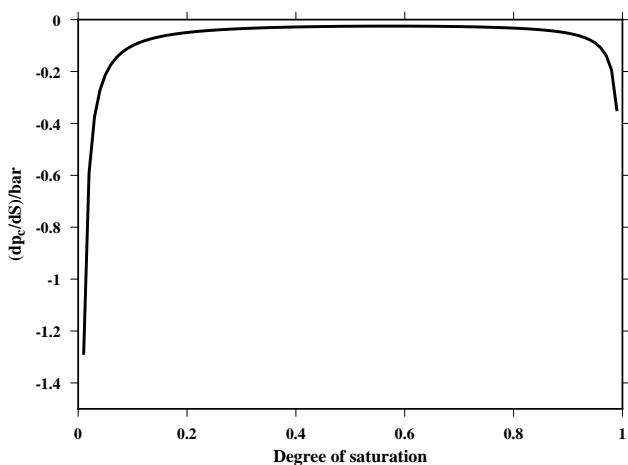


Figure 9. Partial derivative of capillary pressure with respect to degree of saturation for drainage by the sand sample studied by *She and Sleep* [1998].

Figure 9. Partial derivative of capillary pressure with respect to degree of saturation for drainage by the sand sample studied by *She and Sleep* [1998].

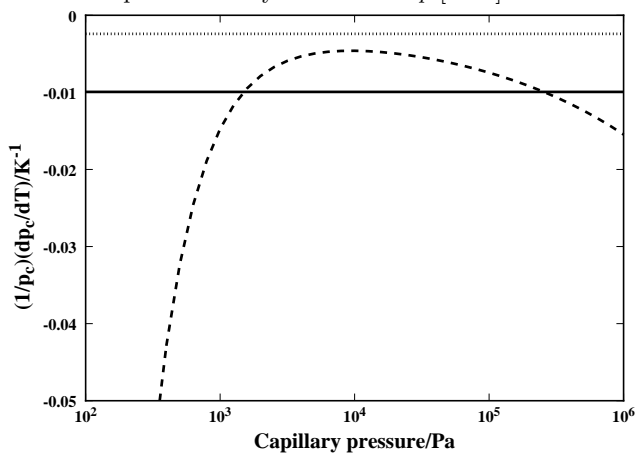


Figure 10. Plot of three elements of equation (10). Solid line: $(1/p_c)(dp_c/dT)$; dashed line: $(1/p_c)(\partial p_c/\partial \theta)(\partial \theta/\partial T)$; stippled line: $(1/\gamma^{ls})(d\gamma^{ls}/dT)$.

Figure 10. Plot of three elements of equation (10). Solid line: $(1/p_c)(dp_c/dT)$; dashed line: $(1/p_c)(\partial p_c/\partial \theta)(\partial \theta/\partial T)$; stippled line: $(1/\gamma^{ls})(d\gamma^{ls}/dT)$.

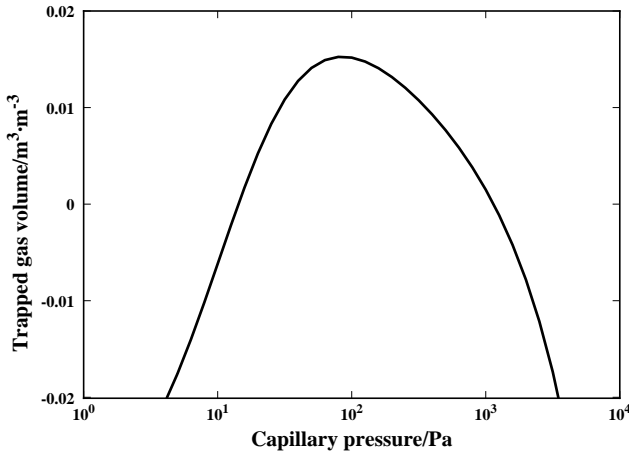


Figure 11. Predicted volumes of entrapped air of a Plano sandy loam as a function of capillary pressure for the model of *Peck* [1960] for the effect of temperature on capillary pressure to be consistent with the empirically determined value of β_0 .

Figure 11. Predicted volumes of entrapped air of a Plano sandy loam as a function of capillary pressure for the model of *Peck* [1960] for the effect of temperature on capillary pressure to be consistent with the empirically determined value of β_0 .

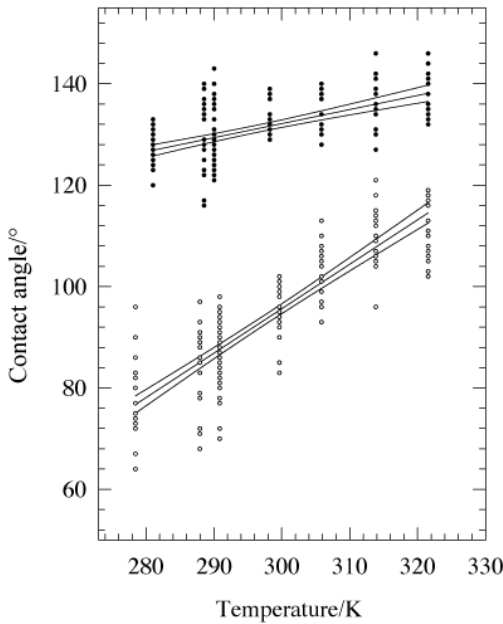


Figure 12. Sessile drop contact angle measured on hydrophobic soil particles of the silt fraction. Soil was treated with 84 mL dimethyldichlorosilane per kg dry soil (closed symbols) and 21 mL silane per kg soil (open symbols). The method was reported by *Bachmann et al.* [2000].

Figure 12. Sessile drop contact angle measured on hydrophobic soil particles of the silt fraction. Soil was treated with 84 mL dimethyldichlorosilane per kg dry soil (closed symbols) and 21 mL silane per kg soil (open symbols). The method was reported by *Bachmann et al.* [2000].

Table 1. Values of β_0 estimated by nonlinear regression analysis of capillary pressure saturation relations in the published literature and the corresponding relative values of the temperature derivative of capillary pressure and this temperature derivative to that of water's surface tension.

Matrix	D/I	$\beta_0 \pm \text{SE}$	$(\frac{1}{p_c})(\frac{dp_c}{dT})$	$\frac{(\frac{1}{p_c})(\frac{dp_c}{dT})}{(\frac{1}{\gamma_{\text{H}_2\text{O}}})(\frac{d\gamma_{\text{H}_2\text{O}}}{dT})}$	Citation
Sand	D	$8.76 \times 10^{139} \pm 0$		0.00	<i>Bachmann</i> [1998]
Hydrophobicized sand	D	$- - 1.51 \times 10^{139} \pm 0$		0.00	<i>Bachmann</i> [1998]
Silt	D	-507.4 ± 26.4	-0.00478	2.24	<i>Bachmann</i> [1998]
Hydrophobicized silt	D	-603.4 ± 57.1	-0.00328	1.53	<i>Bachmann</i> [1998]
Soil	D	-674.3 ± 56.8	-0.00266	1.25	<i>Bachmann</i> [1998]
Hydrophobicized soil	D	-346.6 ± 12	-0.02064	9.67	<i>Bachmann</i> [1998]
Oakley Sand	D	-413.4 ± 15.3	-0.00868	4.06	<i>Constantz</i> [1982]
Oakley Sand (dynamic)	D	-419.7 ± 13	-0.00823	3.85	<i>Constantz</i> [1982]
Hanford					
Sandy Loam	D	-441.2 ± 36	-0.00699	3.27	<i>Constantz</i> [1982]
Hanford					
Sandy Loam (dynamic)	D	-448.8 ± 16.8	-0.00664	3.11	<i>Constantz</i> [1982]
Tipperary Sand	D	-498.2 ± 27.7	-0.00500	2.34	<i>Constantz</i> [1983]
Tipperary Sand	I	-440.4 ± 15.9	-0.00703	3.29	<i>Constantz</i> [1983]
Nonwelded tuff	D	-441 ± 17.2	-0.00700	3.28	<i>Constantz</i> [1991]
Nonwelded tuff	I	-598.1 ± 89.5	-0.00333	1.56	<i>Constantz</i> [1991]
Oakley sand	D	-436.2 ± 10.8	-0.00724	3.39	<i>Constantz</i> [1991]
Oakley sand	I	-391.8 ± 4.4	-0.01068	5.00	<i>Constantz</i> [1991]
Quartz sand	D	-783.9 ± 48	-0.00206	0.96	<i>Crausse</i> [1983]
Mixed sand	D	-384.2 ± 10.7	-0.01162	5.44	<i>Davis</i> [1994]
Mixed sand	I	-812.3 ± 612	-0.00194	0.91	<i>Davis</i> [1994]
Standard sand	D	-386.1 ± 6.7	-0.01137	5.33	<i>Davis</i> [1994]
Standard sand	I	$- - 4 \times 10^{12} \pm 0$		0.00	<i>Davis</i> [1994]
Loam	I	-376.6 ± 12	-0.01275	5.97	<i>Faybishenko</i> [1983]
Loam	I	-381.9 ± 10.7	-0.01194	5.59	<i>Faybishenko</i> [1983]
silt loam	D	-437.8 ± 21.2	-0.00716	3.35	<i>Haridasan and Jensen</i> [1972]
Dundee					
silt loam	D	-566 ± 62.8	-0.00373	1.75	<i>Haridasan and Jensen</i> [1972]
Norfolk					
sandy loam	D	-439.3 ± 29.7	-0.00708	3.32	<i>Hopmans and Dane</i> [1986b]
Norfolk					
sandy loam	I	-370.6 ± 13.2	-0.01380	6.46	<i>Hopmans and Dane</i> [1986b]
Subalpine clay loam	D	-385.4 ± 13.6	-0.01146	5.37	<i>Meeuwig</i> [1964]
Mountain brush zone clay loam	D	-355.4 ± 14.1	-0.01747	8.18	<i>Meeuwig</i> [1964]
Millville silt loam	D	-522.7 ± 45.5	-0.00445	2.09	<i>Meeuwig</i> [1964]
Glass beads	D	-450.8 ± 1.5	-0.00655	3.07	<i>Nimmo and Miller</i> [1986]
Glass beads	I	-403.9 ± 1	-0.00946	4.43	<i>Nimmo and Miller</i> [1986]
Plainfield sand	D	-431.5 ± 5	-0.00750	3.51	<i>Nimmo and Miller</i> [1986]
Plainfield sand	I	-414.5 ± 3.8	-0.00859	4.03	<i>Nimmo and Miller</i> [1986]
Plano silt loam	D	-395.8 ± 3.5	-0.01024	4.80	<i>Nimmo and Miller</i> [1986]
Plano silt loam	I	-333.5 ± 1.6	-0.02829	13.25	<i>Nimmo and Miller</i> [1986]
Granular glass	D	-388.8 ± 9.7	-0.01103	5.17	<i>Novák</i> [1975]
Glass beads	?	-878.9 ± 18.4	-0.00172	0.81	<i>Salehzadeh</i> [1990]
Plano silt loam	D	-380.4 ± 2	-0.01216	5.69	<i>Salehzadeh</i> [1990]

Table 1. (continued)

Matrix	D/I	$\beta_0 \pm \text{SE}$	$(\frac{1}{p_c})(\frac{dp_c}{dT})$	$\frac{(\frac{1}{p_c})(\frac{dp_c}{dT})}{(\frac{1}{\gamma_{\text{H}_2\text{O}}})(\frac{d\gamma_{\text{H}_2\text{O}}}{dT})}$	Citation
Plano silt loam	I	-356 ± 2	-0.01729	8.10	<i>Salehzadeh</i> [1990]
Elk mound sandy loam	D	$-2 \times 10^{15} \pm 0$		0.00	<i>Salehzadeh</i> [1990]
Elk mound sandy loam	I	-398.8 ± 5.9	-0.00994	4.65	<i>Salehzadeh</i> [1990]
Sand	D	-468.8 ± 5	-0.00586	2.74	<i>She and Sleep</i> [1998]
Sand	I	-617.7 ± 59.9	-0.00313	1.47	<i>She and Sleep</i> [1998]
104-149 μm sand	D	-670 ± 30.5	-0.00269	1.26	<i>Wilkinson and Klute</i> [1962]
53-74 μm sand	D	-501.4 ± 8.1	-0.00492	2.30	<i>Wilkinson and Klute</i> [1962]
13.0-18.5 μm silt	D	-522.2 ± 9.4	-0.00446	2.09	<i>Wilkinson and Klute</i> [1962]

EFFECT OF TEMPERATURE ON CAPILLARY PRESSURE

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